

Project ID: **54716**

Project Title: **Polyoxometalates for Radioactive Waste Treatment**

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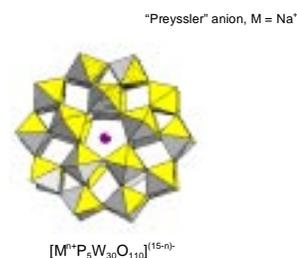
RESEARCH OBJECTIVE

The research project has two major goals: (1) the selective sequestration of lanthanide (Ln) and actinide (An) cations, and technetium species, from tank waste solutions, using radiation-resistant and thermally-stable polyoxometalate anions as complexants, and (2) the conversion of complexed Ln/An/Tc to reduced oxide bronzes (e.g. M_xWO_3) under relatively mild conditions, and evaluation of the use of such bronzes as waste forms.

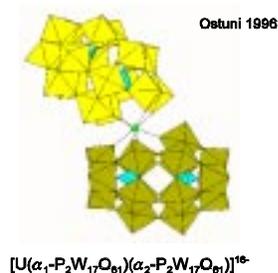
RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes progress after 3 years of a 3-year project; a no-funds extension is requested to enable completion of the original goals.

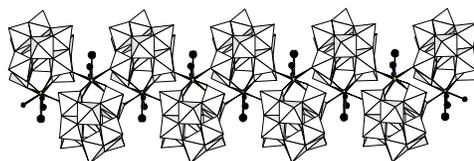
1. Selective sequestration of Ln^{3+}/An^{4+} by $[NaP_5W_{30}O_{110}]^{14-}$ (I). The sodium cation that occupies the central cavity of this doughnut-shaped polyoxotungstate can be replaced only by cations of the same size, i.e. Ln^{3+} , An^{4+} (U → Cm), Ca^{2+} . *Other cations are excluded.* In aqueous solution (neutral or mildly acidic) at 160°, Nd^{3+} for example is incorporated in the presence of the major components of tank wastes, i.e. a 200-fold molar excess of Na^+ , and in presence of Fe^{3+} and Al^{3+} . The encrypted metal cations are released by hydrothermal treatment under strongly acidic conditions.



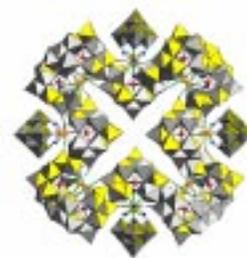
2. New polytungstate complexes of Ln^{3+} and An^{4+} . The conditions of formation, structures, and stabilities of several new polytungstates as possible precursors to thermal conversion to tungsten bronzes (see below) have been determined. These include 1:1 and 1:2 complexes of the lacunary anion ligands $[P_2W_{17}O_{61}]^{10-}$ (II), and some very large assemblies incorporating multiple Ln cations (III, IV, V)



III

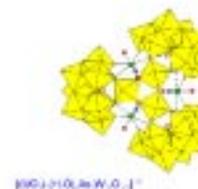


IV



V

3. Polytungstate complexation of UO_2^{2+} . Uranyl (and other actinyl) cations are stable in aqueous solution under normal atmospheric conditions. The first examples of polytungstate complexes of UO_2^{2+} have been synthesized and structurally characterized. Examples include $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ (VI) and $[(UO_2)_3(H_2O)_6As_3W_{30}O_{105}]^{15-}$ (VII). Anion VI is formed in



solutions of high $[\text{Na}^+]$ and is extractable into organic solvents.

VII

4. Conversion of tungstolanthanide and -actinide salts into tungsten bronzes. Under relatively mild conditions (N_2 or H_2 atmosphere, $500\text{-}700^\circ\text{C}$) ammonium salts of anions such as **IV** and **VII** are cleanly converted into the cubic bronzes $(\text{Ln}/\text{An})_x\text{WO}_3$. This method of synthesis represents a major improvement over conventional methods (ground mixtures of oxides and tungsten powder, $\geq 1000^\circ\text{C}$) and is the subject of a patent application. The chemical stability of the bronzes as candidates for potential waste forms is currently under investigation.

5. Technetium recovery and storage. Initial investigations are being carried out with rhenium as a Tc-surrogate. Tungstorhenates incorporating Re(V) and Re(IV) have been characterized but polyniobates and niobotungstates offer the advantages of stability in alkaline solutions which constitute the majority of tank wastes. The first example of a nioborhenate(IV) complex, $[\text{Re}(\text{Nb}_6\text{O}_{19})_2]^{12-}$, has been isolated from alkaline solution but has proved difficult to crystallize for structural confirmation.

PLANNED ACTIVITIES

As indicated above, a no-funds extension of the project is requested in order to complete (1) investigation of the nioborhenate (technetate) and structurally-related niobotungstorhenate complexes, and (2) evaluation of the hydrolytic stability of the Ln/An bronzes. It is estimated that this will require 6-9 months.

INFORMATION ACCESS

www.georgetown.edu/faculty/popem/poster.htm#poster

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2. "Self-Assembly of Supramolecular Polyoxometalates. The Compact, Water-Soluble Heteropolytungstate Anion $[\text{As}^{\text{III}}_{12}\text{Ce}^{\text{III}}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ ", Wassermann, K.; Dickman, M.H.; Pope, M.T., *Angew.Chem.*, **1997**, 109, 1513-1516; *Angew.Chem.Internat.Ed.Engl.*, **1997**, 36, 1445-1448
3. "Compounds and Methods for Separation and Molecular Encapsulation of Metal Ions", Pope, M.T.; Creaser, I.I.; Heckel, M.C., U.S. Patent 5,618,472 (April 8, 1997)
4. "Polyoxometalates: Very Large Structures - Nanoscale Magnets", Müller, A.; Peters, F.; Pope, M.T.; Gatteschi, D., *Chem.Rev.* **1998**, 98, 239-271
5. "New Developments in the Chemistry of Heteropolytungstates of Rhodium and Cerium" Pope, M.T.; Wei, X.; Wassermann, K.; Dickman, M.H., *C.R.Acad.Sci.*, **1998**, 1, Ser.IIc, 297-304
6. "Cation-directed Structure Changes in Polyoxometalate Chemistry. Equilibria between Isomers of Bis(9-tungstophosphatodioxouranate(VI)) Complexes", Kim, K.-C.; Pope, M.T. *J.Am.Chem.Soc.* **1999** accepted

7. "Slow Proton Transfer in Aqueous Solution. Consequences of Protonation and Hydration within the Central Cavity of Preyssler Anion Derivatives, $[M(H_2O)]_cP_5W_{30}O_{110}]^{n-}$ ", Kim, K.-C.; Pope, M.T.; Gama, G.G.; Dickman, M.H. *J.Am.Chem.Soc.* submitted.